

Solid-state NMR and DFT calculations of Dodecahedrane

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Objects with five-fold axes of symmetry are forbidden to express this symmetry in ordered periodic arrays (e.g. crystal lattices) due to their inability for proper space filling without gaps or voids. This restriction is lifted for objects of two-, three-, four-, and six-fold rotational symmetry. It is predictable that dodecahedrane's five membered rings must all undergo a small distortion upon crystallization. This distortion from the ideal is commensurate with eight carbons forming the vertices of an ideal cube within the lattice. Six sets of two adjacent carbons form ethano bridges above the cube's six faces. The X-ray crystallographer finds crystalline dodecahedrane's twenty carbons to reside in two diastereotopic sets in the ratio of eight on-vertex carbons to twelve off-vertex partners of a T_h -symmetry solid skeleton.

The lack of appendages in crystalline spherical molecules enables them to undergo reorientation about their molecular axes which is readily observable by solid state NMR. Thus, at ambient temperature, both S_6 -symmetry crystalline cubane and T_h -symmetry crystalline dodecahedrane exhibit ^{13}C isochrony due to fast topomerization of their diastereotopic nuclei. We herein present the CP-build up rates attesting the mobility differences of lighter cubane versus heavier dodecahedrane. The ^{13}C MAS spectra display line-narrowing with decreasing temperature until relatively narrow signals were observed below 224K. This observation is not consistent with a static T_h -symmetry dodecahedrane geometry.